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L5: Entry 1 of 42

File: USPT

Feb 19, 2002

DOCUMENT-IDENTIFIER: US 6348432 B1

TITLE: Heat sensitive coating, recording material and methods of manufacture

Abstract Paragraph Left (1):

Disclosed are heat sensitive coatings and record materials that are environmentally resistant and therefore do not require a protective coating. One embodiment includes an environmentally resistant heat sensitive coating that includes an acrylate polymer of the formula: ##STR1##

Brief Summary Paragraph Right (3):

Typical heat sensitive coatings are aqueous dispersions of a color former, a color developer, an optional organic sensitizer and a water soluble polymeric binder. The polymeric binder, e.g., polyvinyl alcohol, polyvinylpyrrolidone, or the like, typically is highly soluble in water. Accordingly, heat sensitive layers which contain water soluble polymers, like polyvinyl alcohol, have a high affinity for water such that the resulting recording material may be easily damaged by the presence of moisture. In addition, organic sensitizers and bisphenol-type developers in typical heat sensitive coatings often are soluble in oil such that contact between the recording material and an oil may result in reversal of an image formed by development at the area of contact.

Brief Summary Paragraph Right (4):

Protective coatings generally include water soluble polymer binders such as, for example, polyvinyl alcohol crosslinked with a crosslinker such as, for example, melamine-formaldehyde. These top coat layers tend to reduce the incidence of damage to the recording material by water and/or oil, however, they do not protect the recording material from prolonged exposure to water.

Brief Summary Paragraph Right (5):

The use of a protective coating also increases the cost of the heat sensitive recording material, for example, the costs of the protective coating materials and the processing costs involved in preparing and coating the protective coating are added to the overall costs of the commercial product. Moreover, protective coatings typically reduce the tint strength of the heat sensitive layer due to increased spacing between the thermal head of the thermal printer and the color producing layer when printing. Additionally, protective layers typically include a plastic binder and/or fillers comprising pigment. Plastic binders typically are heat insulating which further reduces the potential tint strength and pigments which tend to mask the developed color of the heat sensitive layer.

Brief Summary Paragraph Right (7):

An environmentally resistant heat sensitive coating of the present invention includes an acrylate polymer of the formula: ##STR3##

Brief Summary Paragraph Right (8):

In one embodiment of the present invention, the acrylate polymer is soluble in an alkaline aqueous solution. In another embodiment, the acrylate polymer is a methylmethacrylate/ethylacrylate/methacrylic acid polymer, a methylmethacrylate/n-butylmethacrylate/methacrylic acid polymer, a methylmethacrylate/methylacrylate/methacrylic acid polymer, a methylmethacrylate/hydroxyethylmethacrylate/methacrylic acid polymer, a methylmethacrylate/hydroxypropylmethacrylate/methacrylic acid polymer, or a methylmethacrylate/propylacrylate/methacrylic acid polymer.

Brief Summary Paragraph Right (9):

In another embodiment, an organic sensitizer is included with the acrylate polymer. Suitable sensitizers include, but are not limited to, polyaromatic waxes, methylbenzyl oxalates, for example, di-p-methylbenzyl oxalate, terphenyls, for example p-terphenyl, benzobiphenyls, fatty acids, fatty acid esters, for example, stearate, fatty amides, for example, stearamide, fatty acid salts, polyethylene waxes, dimethylphenyl ethane, for example, 1,2 bis(3,4-dimethylphenyl)ethane, carnauba waxes, microcrystalline waxes, and carboxy-modified paraffin waxes.

Brief Summary Paragraph Right (15):

Yet another aspect of the present invention is a method of making an environmentally resistant heat sensitive recording which includes the following steps: (a) providing a heat sensitive coating comprising an acrylate polymer of the formula: ##STR5##

Brief Summary Paragraph Right (18):

Generally, the invention disclosed herein includes an environmentally resistant heat sensitive coating including an acrylate polymer of the formula: ##STR7##

Brief Summary Paragraph Right (19):

In one embodiment of the invention, the acrylate polymer is soluble in an alkaline aqueous solution. This solubility is due in part to the presence of carboxylic acid groups, which are neutralized in alkaline aqueous solutions. Without wishing to be bound to any particular theory, it is believed that the acrylate polymers of the present invention, being not readily soluble in neutral and acidic water, increase the resistance of the coating to water damage. Preferably, the acrylate polymer also has a glass transition temperature (Tg) equal to or greater than about 100.degree. C.

Brief Summary Paragraph Right (20):

One polymer suitable for use in accordance with the present invention is methylmethacrylate/ethylacrylate/methacrylic acid. This polymer has a glass transition temperature (Tg) of about 100.degree. C., an average molecular weight of about 60,000, an acid number of about 120, and is soluble in an alkaline aqueous solution. This polymer is commercially available under the trade name Elvacite.TM.-2669 from ICI Co. (Memphis, Tenn.).

Brief Summary Paragraph Right (21):

Another suitable polymer is methylmethacrylate/n-butylmethacrylate/ methacrylic acid with a weight ratio of approximately 70/5/25 respectively. Other acrylate polymers suitable for use in accordance with the present invention include methylmethacrylate/methylacrylate/methacrylic acid polymers, methylmethacrylate/hydroxyethylmethacrylate/methacrylic acid polymers, methylmethacrylate/hydroxypropylmethacrylate/methacrylic acid polymers, and methylmethacrylate/propylacrylate/methacrylic acid polymers

Brief Summary Paragraph Right (22):

Methods of making acrylate polymers by homogeneous free-radical polymerization such as bulk, solution and suspension polymerization are well known to those skilled in the art.

Brief Summary Paragraph Right (23):

In another embodiment of the invention, the heat sensitive coating further includes an organic sensitizer. Without wishing to be bound to any particular theory, it is believed that when the heat sensitive coating is thermally activated to form an image, the acrylate polymer in the presence of the organic sensitizer produces a change in the coating which results in a further improvement in the resistance of the coating and recording material to water, oils and plasticizers.

CLAIMS:

1. An environmentally resistant heat sensitive coating comprising:

a color former selected from the group consisting of fluorans, thiofluoranes, spiropyrans, triarylmethanes, xanthenes, and methynes;

a color developer; and

an acrylate polymer of the formula: ##STR9##

wherein R.sub.1 is a hydrogen or a methyl group, R.sub.2 is a hydrogen or a methyl group, and R.sub.3 is nitrile or chlorine or ##STR10##

wherein, when c is 0, R.sub.4 is methyl, phenyl, or substituted phenyl, and when c is greater than 0, R.sub.4 is methyl, phenyl, substituted phenyl, halogen, nitrite or hydroxyl;

m is greater than 1;

n is greater than 1;

b is greater than or equal to 0; and

c is an integer from 0 to 38.

2. The coating of claim 1 wherein the acrylate polymer is soluble in an alkaline aqueous solution.

3. The coating of claim 1 wherein the acrylate polymer is selected from the group consisting of methylmethacrylate/ethylacrylate/methacrylic acid polymers, methylmethacrylate/n-butylmethacrylate/methacrylic acid polymers, methylmethacrylate/methylacrylate/methacrylic acid polymers, methylmethacrylate/hydroxyethylmethacrylate/methacrylic acid polymers, methylmethacrylate/hydroxypropylmethacrylate/methacrylic acid polymers, and methylmethacrylate/propylacrylate/methacrylic acid polymers.

15. An environmentally resistant heat sensitive recording material comprising:

a substrate; and

a heat sensitive coating comprising:

a color former selected from the group consisting of fluorans, thiofluoranes, spiropyrans, triarylmethanes, xanthenes, and methynes;

a color developer; and

an acrylate polymer of the formula: ##STR11##

wherein R.sub.1 is a hydrogen or a methyl group, R.sub.2 is a hydrogen or a methyl group, and R.sub.3 is nitrile or chlorine or ##STR12##

wherein, when c is 0, R.sub.4 is methyl, phenyl, or substituted phenyl, and when c is greater than 0, R.sub.4 is methyl, phenyl, substituted phenyl, halogen, nitrile or hydroxyl;

m is greater than 1;

n is greater than 1;

b is greater than or equal to 0; and

c is an integer from 0 to 38.

16. The recording material of claim 15 wherein the acrylate polymer is soluble in an alkaline aqueous solution.

17. The recording material of claim 15 wherein the acrylate polymer is selected from the group consisting of methylmethacrylate/ethylacrylate/methacrylic acid polymers, methylmethacrylate/n-butylmethacrylate/methacrylic acid polymers, methylmethacrylate/methylacrylate/methacrylic acid polymers, methylmethacrylate/hydroxyethylmethacrylate/methacrylic acid polymers, methylmethacrylate/hydroxypropylmethacrylate/methacrylic acid polymers, and methylmethacrylate/propylacrylate/methacrylic acid polymers.

29. A method of making an environmentally resistant heat sensitive recording comprising:

(a) providing a heat sensitive coating comprising:

a color former selected from the group consisting of fluorans, thiofluoranes,

spiropyrans, triarylmethanes, xanthenes, and methynes;

a color developer; and

an acrylate polymer of the formula: ##STR13##

wherein R.sub.1 is a hydrogen or a methyl group, R.sub.2 is a hydrogen or a methyl group, and R.sub.3 is nitrite or chlorine or ##STR14##

wherein, when c is 0, R.sub.4 is methyl, phenyl, or substituted phenyl, and when c is greater than 0, R.sub.4 is methyl, phenyl, substituted phenyl, halogen, nitrile or hydroxyl;

m is greater than 1;

n is greater than 1;

b is greater than or equal to 0; and

c is an integer from 0 to 38;

(b) coating a substrate with the heat sensitive coating; and

(c) thermally activating the heat sensitive coating.

30. The method of claim 1 wherein the acrylate polymer is soluble in an alkaline aqueous solution.

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File: USPT

Jul 28, 1998

DOCUMENT-IDENTIFIER: US 5786430 A

TITLE: Thermosetting, powder coating compositions

Abstract Paragraph Left (1):

Thermosetting powder coating compositions include at least one glycidic-ether containing amorphous and/or semi-crystalline copolyester and a cross-linking agent which is an aliphatic and/or cycloaliphatic polybasic acid and/or its anhydride and/or a polyol-modified anhydride of a polybasic acid and/or amorphous or semi-crystalline carboxyl-functional copolyester resins and/or carboxyl-functional acrylate resins.

Brief Summary Paragraph Right (1):

The invention in particular relates to thermosetting powder systems, also called powder coating compositions, with epoxide group-containing amorphous and/or semi-crystalline copolyesters, suitable curing agents and/or pigments and/or fillers and/or additives, wherein the epoxide group-containing amorphous and/or semi-crystalline polyester is one produced by a polymer analogous reaction of hydroxyl-functional copolyesters with epihaloalkanes.

Brief Summary Paragraph Right (6):

These special glycidic ether groups containing amorphous and/or semi-crystalline copolyesters are particularly suitable as binders for thermosetting powder coating systems.

Brief Summary Paragraph Right (9):

(B) an aliphatic and/or cycloaliphatic polybasic acid and/or its anhydride and/or a polyol-modified anhydride of a polybasic acid and/or amorphous or semi-crystalline carboxyl functional copolyester resins and/or carboxyl-functional acrylate resins, and

Brief Summary Paragraph Right (10):

(C) if required or optionally, fillers and/or pigments and/or additives,

Brief Summary Paragraph Right (11):

wherein the glycidic ether-containing amorphous and/or semi-crystalline copolyester has a molecular weight (Mn) of 300 to 10,000 and can be obtained by-providing in a first step, ~~an amorphous and/or semi-crystalline copolyester~~ (D) containing hydroxyl groups, which subsequently is converted in further steps by the reaction with epihaloalkanes into an epoxide group-containing copolyester (A).

Brief Summary Paragraph Right (26):

Examples are adipic acid (poly) anhydride, azelaic acid (poly) anhydride, sebacic acid (poly) anhydride, dodecane dioic acid (poly) anhydride, etc. The polyanhydrides have a molecular weight (average weight in relation to the polystyrene standard) of 1,000 to 5,000. The polyanhydrides can also be modified with polyol. The polyanhydrides can also be employed in a mixture with the aliphatic dibasic dicarboxylic acids, which have melting points between 40.degree. and 150.degree. C., for example 12-hydroxy stearic acid, 2- or 3- or 10-hydroxy octadecanic acid, 2-hydroxy myristic acid.

Brief Summary Paragraph Right (32):

Suitable semi-crystalline polyesters have an acid number of 10 to 400 (mg KOH/g) and an exactly defined DSC melting point. The semi-crystalline polyesters are condensation products from aliphatic polyols, preferably aliphatic diols, and aliphatic and/or cycloaliphatic and/or aromatic polybasic carboxylic acids, preferably dibasic acids. Examples of aliphatic polyols are: ethylene glycol (1,2-ethane diol), propylene glycol (1,3-propane diol), butylene glycol (1,4-butane diol), 1,6-hexane diol, neopentyl glycol, cyclohexane dimethanol, trimethylol propane, etc. Aliphatic diols are

preferred, such as ethylene glycol, butylene glycol and 1,6-hexane diol.

Brief Summary Paragraph Right (34):

Suitable carboxyl-functional acrylate polymers have an acid value number of 10 to 300 (mg KOH/g), produced by copolymerization of a mixture of monomers, consisting of

Brief Summary Paragraph Right (35):

The monomers b) are preferably (cyclo)alkyl esters of acrylic or methacrylic acid with 2 to 18 carbon atoms in the (cyclo)alkyl radical. Examples of suitable or preferably suitable monomers b) are ethyl(methyl)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, tert.-butyl(meth)acrylate, 2-ethyl hexyl(meth)acrylate, cyclohexylmethacrylate, neopentyl methacrylate, isobornylmethacrylate, 3,3,5-trimethyl cyclohexyl methacrylate and stearyl methacrylate.

Brief Summary Paragraph Right (37):

Production of the copolymers can take place by copolymerization of the monomers a) to d) cited by way of example in accordance with customary radical polymerization processes, such as solvent, emulsion, bead or substance polymerization. In this case the monomers are copolymerized at temperatures between 60.degree. to 160.degree. C., preferably 80.degree. to 150.degree. C., in the presence of radical-forming agents and possibly molecular weight regulators.

Brief Summary Paragraph Right (38):

Production of the carboxyl-functional acrylate copolymers takes place in inert solvents. Suitable solvents are, for example, aromatics, such as benzene, toluene, xylene; esters, such as ethyl acetate, butyl acetate, hexyl acetate, heptyl acetate, methylglycol acetate, ethylglycol acetate, methoxypropyl acetate; ethers, such as tetrahydro-furane, dioxane, diethylene glycoldimethyl ether; ketones, such as acetone, methylethyl ketone, methylisobutyl ketone, methyl-n-amyl ketone, methylisoamyl ketone or arbitrary mixtures of such solvents.

Brief Summary Paragraph Right (42):

Usual radical starters are suitable initiators, for example aliphatic azo compounds, such as azodiisobutyric nitrile, azo-bis-2-methylvalero nitrile, 1,1'-azo-bis-1-cyclohexane nitrile and 2,2'-azo-bis-isobutyric alkyl ester; symmetrical diacyl peroxides, such as acetyl, propionyl or butyryl peroxide, benzoyl peroxides substituted with bromo-, nitro-, methyl- or methoxy groups, lauryl peroxides; symmetrical peroxidicarbonates, for example tert. butylperbenzoate; hydroperoxides, such as tert. butyl hydroperoxide, cumene hydroperoxide; dialkyl peroxides, such as dicumyl peroxide, tert. butylcumyl peroxide or di-tert. butyl peroxide. Conventional regulators can be employed during processing to regulate the molecular weight of the copolymers. Cited as examples are mercaptopropionic acid, tert. dodecyl mercaptan, n-dodecyl mercaptan or diisopropyl xanthogenic disulfide. The regulators can be added in amounts between 0.1 to 10 weight-%, relating to the total amount of monomers.

Brief Summary Paragraph Right (45):

The amounts of anhydrides and acids used as the curing agent--component (B)--in relation to the acrylic resin, can vary over a wide range and depend on the number of epoxide groups in the acrylate resin. Generally a mol-ratio of carboxyl groups or anhydride groups to epoxide groups of 0.4 to 1.4:1, preferably of 0.8 to 1.2:1, is selected.

Brief Summary Paragraph Right (46):

The pigments and/or fillers and/or additives usual for producing and using powder coatings can optionally be present in the coating system in accordance with the present invention. Suitable additives from the group of accelerators, flow control and degassing agents, heat, UV and/or HALS (*hindered amine light stabilizer*) stabilizers and/or tribo-additives, as well as matting agents such as waxes, can be used if desired or required.

Brief Summary Paragraph Type 1 (1):

a) 0 to 70 parts by weight of methyl(meth)acrylate,

Detailed Description Paragraph Right (3):

The molecular weight, calculated as the average number from the end group concentration, is approximately 2800.

Detailed Description Paragraph Right (5):

The molecular weight, calculated as the average number from the end group concentration, is approximately 1700.

Detailed Description Paragraph Right (8):

The molecular weight, calculated as the average number from the end group concentration, is approximately 1100.

Detailed Description Paragraph Right (11):

The molecular weight, calculated as the average number from the end group concentration, is approximately 550.

Detailed Description Paragraph Table (1):

TABLE 1					Properties: Examples 1 to 4 Example 1					
Example 2	Example 3	Example 4			Resin No. I II III					
IV OH-No.	[mg KOH/g]	33	60	100	200	<u>Molecular weight</u> (Mn)	2800	1700	1100	550

Detailed Description Paragraph Table (2):

TABLE 2					Properties: Examples 5 to 12 Example 5									
Example 6	Example 7	Example 8			Resin No. V VI VII									
VIII Starting Resin I	II	III	IV	E-No.	[Equiv./100 g]	0.054	0.095	0.150	0.280	<u>Molecular weight</u> (Mn)	2800	1700	1100	550
Example	Example 9	10	11	12										
Starting Resin I	II	III	IV	E-No.	[Equiv./100 g]	0.052	0.097	0.149	0.281	<u>Molecular weight</u> (Mn)	2800	1700	1100	550

CLAIMS:

1. A thermosetting, powder coating composition comprising the following components:

(A) at least one glycidic ether-containing copolyester, which is amorphous, semi-crystalline or a mixture of said amorphous and semi-crystalline copolyesters, said at least one glycidic ether-containing copolyester having a molecular weight (Mn) of 300 to 10,000 and being obtainable by reacting an epihaloalkane with a copolyester containing hydroxyl groups and wherein, said copolyester containing hydroxyl groups is amorphous, semi-crystalline or a mixture of said amorphous and semi-crystalline hydroxyl containing copolyesters;

(B) a curing agent selected from the group consisting of at least one aliphatic polybasic acid, cycloaliphatic polybasic acid, anhydride of said aliphatic polybasic acid, anhydride of said cycloaliphatic polybasic acid, polyol modified anhydride of a polybasic acid, amorphous or semi-crystalline carboxyl functional copolyester resin, carboxyl-functional acrylate resin, and a mixture thereof;

(C) optionally, at least one of a filler, a pigment, another additive, or a mixture thereof.

9. A coating composition in accordance with claim 1 wherein component (B) is a carboxyl-functional acrylate resin having an acid value number of 10 to 300 (mg KOH/g).

16. A method of forming a protective coating on a substrate, comprising applying a powder coating composition in accordance with claim 1 to said substrate and fusing said composition to said substrate.

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File: USPT

Mar 17, 1998

DOCUMENT-IDENTIFIER: US 5728505 A

TITLE: Flexible, aqueous processable, photoimageable permanent coatings for printed circuits

Brief Summary Paragraph Right (5):

The utilization of polymers containing carboxylic acid groups that are subsequently converted to less reactive and less moisture sensitive species is also known. U.S. Pat. No. 4,987,054 discloses a photo-polymerizable formulation yielding improved properties containing an acid copolymeric binder wherein a copolymer structural unit is the half acid/amide of a dicarboxylic acid. The disclosed formulations are used with conventional rigid printed circuit boards, processed with wholly aqueous alkaline solutions and are storage stable. European Patent Application EP 430,175 discloses a photopolymeric system similar to U.S. Pat. No. 4,987,054.

Brief Summary Paragraph Right (6):

International Patent Application WO 93/17368 discloses an aqueous processable, photoimageable, permanent coating for printed circuits comprising (a) a cobinder consisting of a low molecular weight amic acid copolymer and a high molecular weight carboxylic acid-containing copolymer, (b) an acrylated urethane monomer component, (c) a photoinitiator system, and (d) a thermal crosslinking agent. The coating compositions of the present invention, however, do not contain an amic acid copolymer binder component and have reduced tack when compared to the coatings disclosed in WO 93/17368.

Brief Summary Paragraph Type 1 (1):

(a) a cobinder system comprising at least one low molecular weight copolymer binder component having a molecular weight of from 3,000 to 15,000 and containing from 2 to 50% by weight of at least one carboxylic acid containing structural unit and from 50 to 98% by weight of at least one structural unit of the formula ##STR1## wherein R.sub.1 is H, alkyl, phenyl or aryl; R.sub.2 is H, CH.sub.3, phenyl, aryl, --COOR.sub.3, --CONR.sub.4 R.sub.5 or --CN; and R.sub.3, R.sub.4 and R.sub.5 independently are H, alkyl or aryl, which is unsubstituted or substituted with one or more hydroxy, ester, keto, ether or thioether groups; and at least one high molecular weight carboxylic acid containing copolymer binder component having a molecular weight of from 40,000 to 500,000 and containing structural units of the formula ##STR2## wherein R.sub.6 is H, alkyl, --CN, phenyl, alkylphenyl or aryl; R.sub.7 is phenyl, alkylphenyl, aryl, --COOR.sub.8 or --CONR.sub.4 R.sub.5 ; R.sub.8 is H or alkyl; and wherein alkyl contains from 1 to 8 carbon atoms;

Detailed Description Paragraph Right (3):

The cobinder system essential to the invention contains a low molecular weight copolymer binder component containing from 2 to 50% by weight of at least one carboxylic acid-containing structural unit, and from 50 to 98% by weight of at least one structural unit A of the formula: ##STR3## wherein R.sub.1 is H, alkyl, phenyl or aryl, preferably H or CH.sub.3 ; R.sub.2 is H, CH.sub.3, phenyl, aryl, --COOR.sub.3, --CONR.sub.4 R.sub.5 or --CN, preferably phenyl, --COOR.sub.3 or --CONR.sub.4 R.sub.5 ; and R.sub.3, R.sub.4 and R.sub.5 independently are H, alkyl or aryl, which is unsubstituted or substituted with one or more hydroxy, ester, keto, ether or thioether groups, preferably unsubstituted or hydroxy substituted alkyl or aryl groups.

Detailed Description Paragraph Right (4):

The carboxylic acid-containing structural unit of the acid-containing low molecular weight copolymer binder component can be formed from any ethylenically unsaturated carboxylic acid, or carboxylic acid precursor comonomer that subsequently can be reacted to form the acid, and which will polymerize to form the desired low molecular

weight copolymer. Examples of suitable ethylenically unsaturated carboxylic acid or carboxylic acid precursor comonomers include acrylic and methacrylic acids; maleic acid; maleic acid half ester or anhydride; itaconic acid; itaconic acid half ester or anhydride; citraconic acid; citraconic acid half ester or anhydride; and substituted analogues thereof.

Detailed Description Paragraph Right (5):

Particularly preferred ethylenically unsaturated carboxylic acids are acrylic acid and methacrylic acid. The proportion of carboxylic acid-containing structural unit in the low molecular weight copolymer binder ranges from 2 to 50% by weight, and preferably from 5 to 25% by weight.

Detailed Description Paragraph Right (6):

The molecular weight of the carboxylic acid-containing low molecular weight copolymer binder is in the range of 3,000 to 15,000, as measured by Gel Permeation Chromatography (GPC), preferably from 4,000 to 10,000.

Detailed Description Paragraph Right (7):

Suitable comonomers, which form the structural unit A of the carboxylic acid containing low molecular weight copolymer binder include styrene, substituted styrenes, and unsaturated carboxylic acid derivatives, such as, for example, esters and amides of acrylic and methacrylic acids. Methyl methacrylate, ethyl methacrylate, butyl methacrylate, methacrylamide, methyl acrylate, ethyl acrylate, butyl acrylate, acrylamide, hydroxyethyl acrylate, hydroxyethyl methacrylate and styrene are preferred.

Detailed Description Paragraph Right (8):

When the permanent coating is photoprinted, development of the composition requires that the low molecular weight carboxylic acid-containing copolymer binder component contains sufficient acidic or other groups to render the composition processable in aqueous alkaline developer. The coating layer formed from the composition is removed in portions which are not exposed to radiation but is substantially unaffected in exposed portions during development by aqueous alkaline liquids such as wholly aqueous solutions containing 1% sodium or potassium carbonate by weight for a time period of five minutes at a temperature of 40.degree. C.

Detailed Description Paragraph Right (9):

The permanent coating composition of the invention additionally contains at least one high molecular weight carboxylic acid-containing copolymer binder component to modify coated film integrity, adhesion, hardness, oxygen permeability, moisture sensitivity, and other mechanical or chemical properties required during its processing or end use. Suitable high molecular weight copolymer cobinders, which are used in combination with the low molecular weight carboxylic acid containing copolymer binder component, include monomers which form structural units B: ##STR4## wherein R.sub.6 is H, alkyl, --CN, phenyl, alkylphenyl or aryl; R.sub.7 is phenyl, alkylphenyl, aryl, --COOR.sub.8 or --CONR.sub.4 R.sub.5 ; R.sub.8 is H or alkyl; R.sub.4 and R.sub.5 independently are H, alkyl, or aryl which is unsubstituted or substituted with one or more hydroxy, ester, keto, ether, or thioether groups, preferably unsubstituted or hydroxy substituted alkyl or aryl groups.

Detailed Description Paragraph Right (10):

The carboxylic acid-containing structural unit of the acid-containing high molecular weight copolymer binder component can be formed from any ethylenically unsaturated carboxylic acid, or carboxylic acid precursor comonomer that subsequently can be reacted to form the acid, and which will polymerize to form the desired high molecular weight copolymer. Examples of suitable ethylenically unsaturated carboxylic acid or carboxylic acid precursor comonomers include acrylic and methacrylic acids; maleic acid; maleic acid half ester or anhydride; itaconic acid; itaconic acid half ester or anhydride; citraconic acid; citraconic acid half ester or anhydride; and substituted analogues thereof.

Detailed Description Paragraph Right (11):

Preferred comonomers for use in forming the high molecular weight copolymer binder are styrene, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, acrylic acid, methyl acrylate, ethyl acrylate, octylacrylamide, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate and butyl acrylate. Methacrylic and acrylic acids are especially preferred comonomers in the cobinder for aqueous alkaline development. Other suitable high molecular weight carboxylic acid-containing copolymer binders are those comprising

styrene and maleic anhydride/acid/half ester/ester, and substituted analogues thereof.

Detailed Description Paragraph Right (12):

The proportion of the low molecular weight acid-containing copolymer binder component ranges from 2 to 50 weight %, and the proportion of the high molecular weight carboxylic acid copolymer binder component ranges from 50 to 98 weight %, based on the total weight of the cobinder system.

Detailed Description Paragraph Right (13):

The cobinder system of the present invention, comprising low and high molecular weight carboxylic acid-containing copolymer binder components, is critical to obtaining desired properties of the coating composition. The low molecular weight carboxylic acid-containing binder component helps achieve end-use properties, such as encapsulation of circuit patterns without air entrapment, fast development in aqueous carbonate developer, flexibility, adhesion, resistance to environmental conditions, and resistance to alkali etching or plating solutions. The high molecular weight copolymer binder component is required for film integrity and flexibility of the cured film.

Detailed Description Paragraph Right (14):

The present invention does not require the use of polymers containing carboxylic acid groups that are subsequently converted by reactions within the polymer to less reactive and less moisture sensitive species on curing, such as an amic acid copolymer binder containing the half acid/amide of a dicarboxylic acid. Moreover, the invention does not require the use of such an amic acid polymer to obtain adequate adhesion to flexible circuitry, such as to copper, laminate adhesive or polyimide laminate materials. Furthermore, the cobinder system of the present invention does not contain amic acid functionality and avoids a complicating side reaction with the blocked isocyanate used as crosslinking agent, and tends to produce less residue using aqueous developers. In addition, the low molecular weight copolymers of the invention, compared to low molecular weight amic acid polymers, reduce the amount of volatiles that are liberated at curing and soldering temperatures.

Detailed Description Paragraph Right (15):

The use of a low molecular weight copolymer, preferably 5 weight % of the total binder composition, aids in improving encapsulation during lamination, in reducing the development time required and improving adhesion. The low molecular weight copolymer component acts to plasticize the high molecular weight copolymer component. This provides better flow during vacuum lamination and allows encapsulation of circuit patterns without air entrapment. The plasticizing effect also allows the coating composition to develop in a shorter time than is required if the low molecular weight copolymer is not present. Adhesion is improved with the addition of the low molecular weight copolymer and results in better lamination to the substrate. In addition, there is a reduction in the amount of volatiles that are liberated during curing and during high temperature solder exposure when the low molecular weight amic acids are replaced with the low molecular weight carboxylic acid copolymers of the present invention.

Detailed Description Paragraph Right (16):

A preferred cobinder system of the invention comprises an admixture of from 2 to 50% by weight, most preferably from 4 to 45% by weight, of an acid-containing low molecular weight copolymer component having a molecular weight ranging from 3,000 to 15,000, most preferably from 4,000 to 10,000, an acid number of from 5 to 400, most preferably from 30 to 200 and a Tg of less than 50.degree. and preferably less than 25.degree. C. and from 50 to 98% by weight, preferably from 55 to 96% by weight of an acid-containing high molecular weight copolymer component having a molecular weight ranging from 40,000 to 500,000, most preferably from 100,000 to 250,000, an acid number of from 35 to 400, preferably from 50 to 200, and a Tg of 25.degree. to 100.degree. C. preferably from 30.degree. to 55.degree. C. The optimum ratio of low molecular weight copolymer to high molecular weight copolymer ranges from 0.05 to 0.55, preferably from 0.1 to 0.3.

Detailed Description Paragraph Right (17):

A particularly preferred cobinder system of the present invention comprises an admixture of 11.8% by weight of an acid-containing low molecular weight copolymer component having a monomer composition of 92/8 (by weight) ethyl acrylate/acrylic acid, a molecular weight of 7,000, an acid number of 63, and a Tg of -14.degree. C. and 88.2% by weight of an acid-containing high molecular weight copolymer component having a monomer composition of 32/58/10 (by weight) methyl methacrylate/ethyl acrylate/acrylic acid, a molecular weight of 200,000, an acid number of 80, and a Tg of 37.degree. C.

Detailed Description Paragraph Right (19):

An acrylated urethane is an essential component of the photopolymerizable composition, since it imparts increased flexibility to the cured layer and reduced brittleness, when used in the correct proportion with the other essential ingredients of the invention. It is known that many factors influence the properties (e.g. glass transition temperature) and thus performance of urethane structures in a particular application. These factors include diisocyanate type, diol type (i.e. polyester, polyesteramide, polyether), diol molecular weight, codiols (i.e. short chain diols), ratio of diol to codiol, as well as the amount of branching and molecular weight of the resultant polyurethane. Properties after acrylation will vary correspondingly. It is important to choose the proper acrylated urethane and amount of such relative to the other essential ingredients in order to obtain a proper balance of flexibility, toughness and chemical resistance in the permanent coating. The acrylated urethane is present in an amount of from 5 to 30 parts by weight and contains at least one acrylate or methacrylate group.

Detailed Description Paragraph Right (21):

Particularly preferred herein is a urethane diacrylate which is the reaction product of toluene diisocyanate with a polyol with the end isocyanate groups end-capped with hydroxyethyl acrylate.

Detailed Description Paragraph Right (22):

The acrylated urethane may also include diacrylates and triacrylates which are carboxylated to provide acid numbers ranging from 1 to 50 or more and molecular weights ranging from 500 to 5000. Carboxylated urethane diacrylates and triacrylates are particularly advantageous since they provide cleaner development in aqueous basic developer.

Detailed Description Paragraph Right (23):

Suitable comonomers which can be used in combination with the acrylated urethane include the following: 1,5-pentanediol diacrylate, diethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-propanediol diacrylate, decamethylene glycol diacrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylol-propane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyoxyethylated trimethylolpropane triacrylate and trimethacrylate and similar compounds as disclosed in U.S. Pat. No. 3,380,831, 2,2-di(p-hydroxyphenyl)-propane diacrylate, pentaerythritol tetraacrylate, 2,2-di-(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2,2-di-(p-hydroxyphenyl)-propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloxyethyl) ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-acryloxyethyl) ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of tetrachloro-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrachloro-bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of tetrabromo-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrabromo-bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of 1,4-butanediol, triethylene glycol dimethacrylate, trimethylol propane triacrylate, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4- butanetriol trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol dimethacrylate, pentaerythritol trimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,5-pentanediol dimethacrylate, 1,4- benzenediol dimethacrylate, and 1,3,5-triisopropenyl benzene and polycaprolactone diacrylate. Excessive amounts of trifunctional acrylate monomers can result in reduction of required flexibility.

Detailed Description Paragraph Right (24):

A particularly preferred class of comonomers is hydroxy C.sub.1 -C.sub.10 -alkyl acrylate, hexamethylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, polyoxyethylated trimethylolpropane triacrylate, di-(3-acryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl) ether of tetrabromo-bisphenol-A, or methacrylate analogues thereof.

Detailed Description Paragraph Right (34):

According to the present invention, a thermally activated crosslinking agent is used which crosslinks with the reactive functional groups, such as hydroxyl, carboxyl, amide and amine groups which are present in the copolymer binder components and other ingredients in the photoimageable coating composition. The presence of the proper crosslink imparts the capability to withstand molten solder temperature and improves chemical resistance or other mechanical or chemical properties required in the end-use

product.

Detailed Description Paragraph Right (38):

The polyisocyanates may be blocked by various radicals. Examples of suitable blocking components are beta-dicarbonyl compounds, such as malonates, acetoacetates or 2,4-pentanedione, or hydroxamates, triazoles, imidazoles, tetrahydropyrimidines, lactams, oximes, ketoximes, low molecular weight alcohols, or phenols or thiophenols.

Detailed Description Paragraph Right (43):

Although many elastomers may be used in the permanent coating composition, poly(methyl methacrylate-co-butadiene-co-styrene) is preferred. Other organic fillers which may be used include synthetic flexible polymers and rubbers, e.g., butadiene-co-acrylonitrile, acrylonitrile-co-butadiene-co-styrene, methacrylate-co-acrylonitrile-co-butadiene-co-styrene copolymers, and styrene-co-butadiene-co-styrene, styrene-co-isoprene-co-styrene block copolymers; saturated polyurethanes; poly(methylmethacrylate-co-butylacrylate); and the like. Further examples of organic filler components include conventional elastomers as defined on page 232 of "Hach's Chemical Dictionary" Fourth Edition, Edited by J. Grant, McGraw-Hill Book Company, 1972.

Detailed Description Paragraph Right (44):

The permanent coating compositions may also contain other organic fillers or inorganic particulates to modify the mechanical or chemical properties required during processing or end use. Suitable fillers include organic or inorganic reinforcing agents which are essentially transparent as disclosed in U.S. Pat. No. 2,760,863, e.g., organophilic silica bentonite, silica, and powdered glass having a particle size less than 0.4 micrometer; inorganic thixotropic materials as disclosed in U.S. Pat. No. 3,525,615 such as boehmite alumina, clay mixtures of highly thixotropic silicate oxide such as bentonite and finely divided thixotropic gel containing 99.5% silica with 0.5% mixed metallic oxide; microcrystalline thickeners as disclosed in U.S. Pat. No. 3,754,920 such as microcrystalline cellulose and microcrystalline silicas, clays, alumina, bentonite, kalonites, attapulgites, and montmorillonites; finely divided powders having a particle size of 0.5 to 10 micrometers as disclosed in U.S. Pat. No. 3,891,441 such as silicon oxide, zinc oxide, and other commercially available pigments; and the binder-associated, transparent, inorganic particles as disclosed in European Patent Application 87113013.4 such as magnesium silicate (talc), aluminum silicate (clay), calcium carbonate and alumina. Typically, the filler is transparent to actinic radiation to preclude adverse effects during imaging exposure. Depending on its function in the photopolymerizable composition, the filler may be colloidal or have an average particle size of 0.5 micrometers or more in diameter.

Detailed Description Paragraph Right (46):

Other compounds conventionally added to photopolymer compositions may also be present in the permanent coating to modify the physical properties of the film. Such components include: thermal stabilizers, colorants such as dyes and pigments, coating aids, wetting agents, release agents, and the like.

Detailed Description Paragraph Right (48):

Various dyes and pigments may be added to increase the visibility of the resist image. Any colorant used, however, should preferably be transparent to the actinic radiation used.

Detailed Description Paragraph Right (49):

On the basis of the essential ingredients (a) a cobinder system containing a low molecular weight copolymer component having acid functionality and a high molecular weight carboxylic acid-containing copolymer; (b) acrylated urethane; (c) photoinitiator system; and (d) blocked polyisocyanate crosslinking agent, a suitable concentration is component (a) 20 to 80 parts by weight, component (b) 10 to 40 parts by weight, component (c) 0.5 to 10 parts by weight, and component (d) 5 to 25 parts by weight.

Detailed Description Paragraph Right (70):

Examples 1 to 4 illustrate the properties of coating compositions containing different low MW copolymer binder components having different molecular weights and acid numbers.

Detailed Description Paragraph Right (71):

Examples 5 to 10 illustrate the properties of coating compositions containing different high MW copolymer binders having different T.sub.g and acid numbers.

Detailed Description Paragraph Table (1):

Co-Binders A. High MW copolymers Carboset .RTM. 525 Acrylic acid-containing copolymer from B. F. Goodrich, Cleveland, OH. The T.sub.g is 37.degree. C., the molecular weight is 200M and the acid number is 80 Carboset .RTM. 526 Acrylic acid-containing copolymer from B. F. Goodrich, Cleveland, OH. The T.sub.g is 70.degree. C., the molecular weight is 180M and the acid number is 100 Acrylic polymer #1 Copolymer of methyl methacrylate, ethyl acrylate and acrylic acid (61.7/25.7/12.6) having a T.sub.g of 80.8.degree. C., molecular weight (M.sub.w) of 171M and acid number of 91.0 Acrylic polymer #2 Copolymer of methyl methacrylate, ethyl acrylate and acrylic acid (32/58/10) having a T.sub.g of 35.4.degree. C., molecular weight (M.sub.w) of 168M and acid number of 71.8 Acrylic polymer #3 Copolymer of methyl methacrylate, ethyl acrylate and acrylic acid (32/56.7/11.3) having a T.sub.g of 34.9.degree. C., molecular weight (M.sub.w) of 226M and acid number of 84.6 Acrylic polymer #4 Copolymer of methyl methacrylate, ethyl acrylate and acrylic acid (32/55.4/12.6) having a T.sub.g of 37.3.degree. C., molecular weight (M.sub.w) of 191M and acid number of 90.4 Acrylic polymer #5 Copolymer of methyl methacrylate, ethyl acrylate and acrylic acid (46.8/41.9/11.3) having a T.sub.g of 55.0.degree. C., molecular weight (M.sub.w) of 179M and acid number of 81.5 B. Low MW polymers Carboset .RTM. 515 Acrylic acid containing copolymer having a T.sub.g of -14.degree. C., a molecular weight of 7000 and an acid number of 63 from B. F. Goodrich, Cleveland, OH Low MW copolymer #1 Copolymer of ethyl acrylate and acrylic acid (83/17) having a T.sub.g of 2.3.degree. C., a molecular weight (M.sub.w) of 6400, and an acid number of 117 Low MW copolymer #2 Copolymer of ethyl acrylate and acrylic acid (87/13) having a T.sub.g of -0.8.degree. C., a molecular weight (M.sub.w) of 6500, and an acid number of 102 Low MW copolymer #3 Copolymer of ethyl acrylate, acrylic acid and methyl methacrylate (73/17/10) having a T.sub.g of 12.4.degree. C., a molecular weight (M.sub.w) of 8600, and an acid number of 114 Monomers Ebecryl .RTM. 3704 Diacrylate of bisphenol-A- diglycidyl ether from UBC Chemicals, Smyrna, GA. Ebecryl .RTM. 6700 Urethane diacrylate from UBC Chemicals, Smyrna, GA. Purelast .RTM. 153 Urethane diacrylate from Polymer Systems Corp., Orlando, FL. Purelast .RTM. 159 Carboxylated urethane diacrylate from Polymer Systems Corp., Orlando, FL. Thermal Crosslinking Agents Blocked isocyanate #1 Hexamethylene diisocyanate based polyisocyanate blocked with methyl ethyl ketoxime and dissolved at 75% solids in propylene glycol methyl ether acetate Blocked isocyanate #2 Hexamethylene diisocyanate based polyisocyanate blocked with methyl ethyl ketoxime and dissolved at 75% solids in ethyl acetate Initiators o-Cl HABI Hexaarylbiimidazole EMK Ethyl Michler's Ketone Detackifiers PVP K-120 Polyvinylpyrrolidone from GAF Chemicals Corp., Texas City, TX. Other Ingredients Irganox .RTM. 1010 Antioxidant from Ciba Geigy Corp., Ardsley, NY DayGlo .RTM. HMO15A19 Green dye from Dayglo Corp., Cleveland, OH. DayGlo .RTM. 122-10321 Blue dye from Dayglo Corp., Cleveland, OH. Cobratec .RTM. CBT A 50/50 mixture of 4 & 5 substituted isomers of carboxybenzotriazole from Specialties Group Inc., Cincinnati, OH. 3MT 3-mercapto-1H-1,2,4-triazole from Esprit Chemical Co., Rockland, MA. 5-ATT 5-amino-1,3,4-thiadiazole-2- thiol Cyprubond .RTM. Talc 1726 talc filler from Whittaker, Clark and Daniels, Inc., Plainfield, NJ Claytone .RTM. APA Alkyl quaternary ammonium montmorillonite from Southern Clay Products, Inc., Gonzales, TX

CLAIMS:

1. Coating composition which photopolymerizable-coating-composition which maintains flexibility after curing and is processable in aqueous alkaline developer solution providing a protective coating for printed circuits, which comprises:

(a) a cobinder system comprising at least one low molecular weight copolymer binder component having a weight average molecular weight of from 3,000 to 15,000 and containing from 2 to 50% by weight of at least one carboxylic acid containing structural unit and from 50 to 98% by weight of at least one structural unit of the formula ##STR6## wherein R.sub.1 is H, alkyl or aryl; R.sub.2 is H, CH.sub.3, aryl, --COOR.sub.3, --CONR.sub.4 R.sub.5 or --CN; and R.sub.3, R.sub.4 and R.sub.5 independently are H, alkyl, aryl, or aryl substituted with one or more hydroxy, ester, keto, ether or thioether groups; and at least one high molecular weight carboxylic acid containing copolymer binder component having a weight average molecular weight of from 40,000 to 500,000 and containing structural units of the formula ##STR7## wherein R.sub.6 is H, alkyl, --CN or aryl; R.sub.7 is aryl, --COOR.sub.8 or --CONR.sub.4 R.sub.5 ; and R.sub.8 is H or alkyl containing from 1 to 8 carbon atoms; wherein said low molecular weight and said high molecular weight binder components are present in admixture of differing constituents;

(b) an acrylated urethane monomeric component;

(c) a photoinitiator or a photoinitiator system; and

(d) a blocked polyisocyanate crosslinking agent.

2. The photopolymerizable coating composition of claim 1 wherein the carboxylic acid-containing structural unit of the low molecular weight copolymer binder comprises the polymerized reaction product of an ethlenically unsaturated carboxylic acid.

5. The photopolymerizable coating composition of claim 1 wherein the carboxylic acid structural unit comprises from 5 to 25% by weight of the low molecular weight copolymer binder.

6. The photopolymerizable coating composition of claim 1 wherein the structural unit (A) of the low molecular weight copolymer binder comprises the polymerized reaction product of styrene and esters or amides of acrylic and methacrylic acid.

7. The photopolymerizable coating composition of claim 6 wherein structural unit (A) of the low molecular weight copolymer binder comprises the polymerized reaction product of methyl methacrylate, ethyl methacrylate, butyl methacrylate, methacrylamide, methyl acrylate, ethyl acrylate, butyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, acrylamide, or styrene.

8. The photopolymerizable coating composition of claim 1 wherein the structural units (B) of the high molecular weight carboxylic acid-containing copolymer binder component comprise the polymerized reaction product of styrene, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, octylacrylamide, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate or t-butylaminoethyl methacrylate.

10. The photopolymerizable coating composition of claim 1 wherein the high molecular weight carboxylic acid copolymer binder comprises a copolymer of methyl methacrylate, ethyl acrylate and methacrylic acid.

11. The photopolymerizable coating composition of claim 1 wherein the low molecular weight carboxylic acid copolymer binder comprises a copolymer of ethyl acrylate and acrylic acid.

12. The photopolymerizable coating composition of claim 1 wherein the high molecular weight carboxylic acid copolymer binder comprises a copolymer of styrene and maleic anhydride, acid, ester, half-ester or half-amide.

13. The photopolymerizable coating of claim 1 comprising from 2 to 50% by weight of the low molecular weight copolymer binder component and from 50 to 98% by weight of the high molecular weight carboxylic acid copolymer binder component, based on the total weight of the cobinder system.

14. The photopolymerizable coating of claim 13 comprising from 4 to 45% by weight of the low molecular weight copolymer binder component and from 55 to 96% by weight of the high molecular weight carboxylic acid copolymer binder component.

15. The photopolymerizable coating of claim 14 wherein the low molecular weight copolymer binder component has a molecular weight ranging from 4,000 to 10,000 and the high molecular weight copolymer binder component has a molecular weight ranging from 100,000 to 250,000.

16. The photopolymerizable coating of claim 15 wherein the ratio of the low molecular weight copolymer binder component to the high molecular weight copolymer binder component ranges from 0.05 to 0.55.

17. The photopolymerizable coating of claim 15 wherein the low molecular weight binder component comprises a copolymer of ethyl acrylate and acrylic acid and the high molecular weight binder component comprises a copolymer of methyl methacrylate, ethyl acrylate and acrylic acid.

19. The photopolymerizable coating composition of claim 18 wherein the acrylated urethane monomeric component is a urethane diacrylate comprising the reaction product of toluene diisocyanate with a polyol and the end isocyanate groups end-capped with hydroxyethyl acrylate.

20. The photopolymerizable coating composition of claim 18 wherein the acrylated urethane monomeric component is a urethane triacrylate comprising the reaction product of toluene diisocyanate with a polyol and the end isocyanate groups end-capped with hydroxyethyl acrylate.

23. The photopolymerizable coating composition of claim 1 wherein the blocked polyisocyanate crosslinking agent comprises an aliphatic, cycloaliphatic, aromatic or arylaliphatic di, tri or tetraisocyanate whose isocyanate groups are blocked by betacarbonyl compounds, hydroxamates, triazoles, imidazoles, tetrahydropyrimidines, lactams, ketoximines, oximes, low molecular weight alcohols, phenols or thiophenols.